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## (54) Lubricating oil compositions.

(57) A lubricating oil composition having excellent defoamability, which includes as an essential component a perfluoro ether in an amount by weight of 1-1000 ppm based on the total weight of the composition.

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# LUBRICATING OIL COMPOSITIONS

This invention relates to lubricating oil compositions and more particularly to lubricating oil compositions rich have excellent defoamability (defoaming ability) and are utilizable as engine oils, gear oils, hydraulic oils, automatic transmission oils, bearing oils or the like.

Generally, lubricating oils are made to circulate through lubricating portions (which are those to be lubricated) during their use to save the amount thereof used. Therefore. the oils which passed through the lubricating portions are then returned to a sump. Since the oils have air caught therein at the lubricating portions, the oils so returned ordinarily foam or bubble. If the foam in the oils is difficultly breakable, it will gradually increase during the use of the oils whereupon the oils will finally overflow the sump. Accordingly, defoamability is required in lubricating oils.

Antifoaming agents, such as silicone oils and polyacrylates, have heretofore been added to base oils for the sake of improving the resulting lubricating oils in defoamability.

Although silicone oils are known as good antifoaming agents, they have comparatively high solubility to light-fraction oils thereby they will remarkably lower in defoamability when used in the light-fraction oils. Further, the silicone oils will deteriorate when used for a long period of time, used under hard conditions or used with certain chemical materials, thereby causing the silicone oils to lose their defoamability.

Polyacrylates are inferior in defoamability.

On the other hand, although perfluoro ethers are known as base oils for synthetic lubricating oils, they have never been used as minor components in lubricating oils since they are hardly soluble in other mineral oils and synthetic oils.

Accordingly, it is desired to develop an antifoaming agent which solves the above problems.

The present invention has an object to provide a lubricating oil composition having excellent defoamability or defoaming ability which is little lowered even if the composition is used for a long period of time or under hard conditions.

The present inventors had made intensive studies in attempts to achieve the object mentioned above and, as the result of their studies, they found that a lubricating oil composition including a perfluoroalkyl ether has excellent defoamability. The present invention is based on this finding.

The lubricating oil composition of the present invention includes as an essential component a perfluoro ether in an amount by weight of 1-1000 ppm based on the total weight of the composition.

The present invention will be further explained in detail.

All binds of base oils ordinarily used for lubricating oils are utilizable as base oils used in the lubricating oil compositions of the present invention, and it does not matter whether said base oils are mineral oil-based or synthetic oil-based ones.

Examples of the mineral oil-based lubricating oils used herein are those produced by subjecting fractions obtained by atmospheric distillation or reduced pressure distillation of mineral oils, to any suitable refining treatment such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrodewaxing, sulfuric acid treatment, clay treatment, hydrorefining or the like, or any suitable combination thereof.

Further, examples of the synthetic oil-based lubricating oils include alpha-olefin oligomers such as normal paraffin, isoparaffin, polybutene, polyisobutylene and 1-decene oligomers: alkylbenzenes such as a monoalkylbenzene, dialkylbenzene and polyalkylbenzene; alkylnaphthalenes such as a monoalkylnaphthalene, dialkylnaphthalene and polyalkylnaphthalene; diesters such as di-2-ethylhexyl sebacate, dioctyl adipate, diisodecyl adipate, ditridecyl adipate and ditridecyl glutarate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate and pentaerythritol pelargonate; polyglycols such as polyethylene glycol, polyethylene glycol monoether, polypropylene glycol and polypropylene glycol monoether; polyphenyl ethers; tricresyl phosphate; and silicone oils.

In the present invention, these oils may be used singly or jointly.

The base oils mentioned above should have a viscosity at 40° C of preferably 2 to 1000 centistokes.

Perfluoro ethers having various chemical structures can b⁻ used as an essential component in the lubricating oil composition of the present invention. The perfluoro ethers may be any compound represented by the general formula $R_1\text{-}O\{R_3\text{-}O\}_nR_2$ or may be a mixture thereof.

In the above general formula, $R_1$ and $R_2$ may be identical with, or different from, each other and each represent a straight-chain or branched-chain perfluoralkyl group having 1-4 carbon atoms, $R_3$ represents a straight-chain or branched-chain perfluoroalkylene group having 1-4 carbon atoms, and n is an integer of 2 or more, preferably 10-300. Each of $R_1$ and $R_2$ is exemplified by perfluoromethyl group, perfluoroethyl group, perfluoropropyl group, iso-perfluoropropyl group, perfluorobutyl group, iso-perfluorobutyl group, sec.-

perfluorobutyl group, tert.-perfluorobutyl group or the like. Further, $R_3$ is exemplified by perfluoromethylene group, perfluoroethylene group, perfluorotrimethylene group, perfluoropropylene group, perfluorotetramethylene group, perfluorobutylene group, perfluoro 1,2-dimethylethylene group, perfluoro 1-methyltrimethylene group, perfluoro 2-methyltrimethylene group or the like.

The perfluoro ether used in the present invention may contain different perfluoroalkylene groups in the molecule. In this case, the different perfluoroalkylene groups may form a random copolymer or a block copolymer.

The viscosity of the perfluoro ether used in the present invention is not particularly limited, but it is in the range of usually 10-10000 cSt at 20°C, preferably 20-2000 cSt at 90°C. Further, the average molecular weight of the perfluoro ether is not particularly limited, but it is in the range of usually 500-50000, preferably 1800-10000.

It is important that the lubricating oil composition of the present invention include the perfluoro ether in an amount by weight of 1-1000 ppm, preferably 3-100 ppm, based on the total weight of the composition. In a case where the content of the perfluoro ether in such a lubricating oil composition is less than 1 ppm by weight, the perfluoro ether will undesirably not exert a satisfactory defoaming effect , while in a case where the content of the perfluoro ether exceeds 1000 ppm by weight in such a lubricating oil composition, the perfluoro ether may undesirably be sedimented to be separated from the composition.

The lubricating oil compositions of the present invention may further include, as required, known additives for the purpose of further improving them in properties or performances. Such additives include, for example, antioxidants, detergent-dispersants, viscosity index improvers, pour point depressants, oiliness improvers, wear resistant agents, extreme pressure agents, corrosion inhibitors, metal-deactivators, antifoaming agents (except for the perfluoro ethers mentioned above), emulsifiers, demulsifiers, bactericides and colorants. These various additives are described in detail, for example, in "Junkatsuyu Gakkaishi (Japanese Journal of Lubricating Oil Society), Vol.15, No.6" and "Sekiyuseihin Tenkazai (Additives For Petroleum Products" written by Toshio Sakurai and published by Saiwai Bookstore. These additives may suitably be selected depending on the purpose for which the resulting lubricating oil is used. The lubricating oil compositions of the present invention are also superior in the respect that the perfluoro ethers which are the essential components of said compositions will be less deteriorated by interaction with other additives to be used therewith than the heretofore known antifoaming agents, thereby to enable a wider-range selection of the other additives.

The total amount of these various additives used is ordinarily up to 50% by weight, preferably up to 30% by weight, based on the total weight of the composition.

The lubricating oils of the present invention may be used as engine oils such as a four-cycle gasoline engine oil, land diesel engine oil, marine diesel engine oil and gas engine oil; turbine oils such as an industrial turbine oil, marine turbine oil and gas turbine oil; gear oils such as an automobile gear oil, industrial gear oil and automatic transmission oil; hydraulic oils; compressor oils; vacuum pump oils; refrigerator oils; metal working oils such as a cutting oil, grinding oil, rolling oil, pressing oil, drawing oil, throttling-ironing oil and forging oil; slide guiding surface oils; bearing oils; and the like.

The lubricating oil compositions of the present invention contain a certain small amount of the perfluoro ethers whereby they can be excellent ones which are featured as follows:

(1) The present lubricating oil compositions enable the foaming a light-fraction oil as their base oil to be prevented ;

(2) They exhibit less reduction in defoamability due to the degradation thereof, thereby to lessen the oil change frequency and achieve the cost reduction; and

(3) They can include therein additives which have heretofore been unable to be used for lubricating oils because of degrading silicone oils.

This invention will be better understood by the following Examples and Comparative Examples.

## Example 1 and Comparative Example 1

A perfluoro ether (trade name, Fomblin Y25: viscosity, 250 cSt at 20°C: molecular weight, 3000: produced by Asahi Glass Co., Ltd.) was added in an amount by weight of 30 ppm based on the total oil, to an industrial bearing oil as the base oil (mineral oil-based base oil whose viscosity was 220 cSt at 40°C) to obtain a lubricating oil composition (Example 1), while a silicone oil (viscosity: 3000 cSt at 95°C), instead of the perfluoro ether, was added in an amount by weight of 30 ppm based on the total oil, to the same industrial bearing oil as in Example 1 to obtain a lubricating oil composition (Comparative Example 1). The thus obtained lubricating oil compositions were subjected to the following oxidizing test and then to the

following foaming test, respectively. The test conditions are indicated below, and the results of the foaming test ar indicated in Table 1.

(Oxidizing Test)

The oil compositions were each subjected to oxidition at 150° C for 120 hours in accordance with JIS K 2514 3.1.

(Foaming Test)

A foaming test was carried out on each of the oxidized oil compositions at 24° C in accordance with JIS K 2518.

Table 1

| | Degree of foaming (mℓ) | Stability of foam (mℓ) |
|---|---|---|
| Example 1 | 30 | 0 |
| Comparative Example 1 | 560 | 20 |

Example 2 and Comparative Example 2

A perfluoro ether (trade name, Fomblin Y45: viscosity, 250 cSt at 20° C: molecular weight, 3000: produced by Asahi Glass Co., Ltd.) was added in an amount by weight of 30 ppm based on the total oil, to an automobile transmission oil as the base oil (mineral oil-based base oil whose viscosity is 14 cSt at 100° C) to obtain a lubricating oil composition (Example 2), while a polyacrylate instead of the perfluoro ether was added in an amount by weight of 200 ppm based on the total oil, to the same automobile transmission oil as in Example 2 to obtain a lubricating oil composition (Comparative Example 2). The thus obtained lubricating oil compositions were subjected to the following oxidizing test and then to the same foaming test as in Example 1, respectively. The oxidizing test conditions are indicated hereunder, and the results of the foaming test are indicated in Table 2.

(Oxidizing Test)

The oil compositions were each subjected to oxidation at 150° C for 100 hours in accordance with JIS K 2514 3.1.

Table 2

| | Degree of foaming (mℓ) | Stability of foam (mℓ) |
|---|---|---|
| Example 2 | 20 | 0 |
| Comparative Example 2 | 130 | 0 |

**Claims**

1. A lubricating oil composition including as an essential component a perfluoro ether in an amount by weight of 1-1000 ppm based on the total weight of the composition.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 31 0807

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| X | FR-A-2 099 935 (MONTECATINI)<br>* Claim 1; page 4, line 39 - page 5, line 6; page 7, lines 5-9 * | 1 | C 10 M 147/04<br>C 10 M 171/00 |
| X | CHEMICAL ABSTRACTS, vol. 102, no. 16, April 1985, page 164, abstract no. 134813a, Columbus, Ohio, US;<br>& DD-A-213 944 (VEB PETROLCHEMISCHES KOMBINAT SCHWEDT) 26-09-1984 | 1 | |
| P,Y | EP-A-0 337 425 (AUSIMONT)<br>* Whole document * | 1 | |
| Y | PATENT ABSTRACTS OF JAPAN, vol. 9, no. 134 (C-285)[1857], 8th June 1985;<br>& JP-A-60 22 907 (NIPPON MEKTRON K.K.) 05-02-1985 | 1 | |
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| Y | PATENT ABSTRACTS OF JAPAN, vol. 8, no. 93 (C-220)[1530], 27th April 1984;<br>& JP-A-59 12 708 (NIPPON MEKTRON K.K.) 23-01-1984 | 1 | |
| A | PATENT ABSTRACTS OF JAPAN, vol. 8, no. 106 (C-223)[1543], 18th May 1984;<br>& JP-A-59 22 611 (NIPPON MEKTRON K.K.) 04-02-1984 | 1 | TECHNICAL FIELDS SEARCHED (Int. Cl.5)<br>C 10 M<br>B 01 F<br>B 01 D |

The present search report has been drawn up for all claims

| Place of search | Date of completion of search | Examiner |
|---|---|---|
| The Hague | 21 December 90 | DE LA MORINERIE B.M. |

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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E: earlier patent document, but published on, or after the filing date
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L: document cited for other reasons

&: member of the same patent family, corresponding document